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NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY

[Hisui Denkaishitsu Niji Denchi]

Shuji Ito, Masaki Hasegawa, Yusuke Murai, Yasuhiko Mito, and

Yoshinori Toyoguchi

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Inventor : Shuji Ito, Masaki Hasegawa, Yusuke
Murai, Yasuhiko Mito, and
Yoshinori Toyoguchi

Applicant : Matsushita Electric Industrial
Co., Ltd.

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(54) Title of the invention

NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY

(57) Summary

Objective: To provide a non-aqueous electrolyte secondary battery which exhibits excellent recharge & discharge cycle performances.

Constitution: An Al-Si-Fe alloy which is capable of storing and releasing lithium in a reversible fashion is used as a cathode.

Patent Claims

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Claim 1

A non-aqueous electrolyte secondary battery characterized by the possession of a rechargeable and/or dischargeable anode, a non-aqueous electrolyte, and a cathode which includes an Al-Si-Fe alloy that is capable of storing and releasing lithium in a reversible fashion.

Claim 2

A non-aqueous electrolyte secondary battery specified in Claim 1 wherein the aforementioned cathode is constituted by a mixture which includes said Al-Si-Fe alloy, a carbonaceous material, and a binder.

¹ Numbers in the margin indicate pagination in the foreign text.

Claim 3

A non-aqueous electrolyte secondary battery specified in Claim 1 or 2 wherein the Si internalization ratio and Fe internalization ratio of the aforementioned Al-Si-Fe alloy are 1 ~ 50 wt% and 0.1 ~ 8 wt%, respectively.

Detailed explanation of the invention

[0001]

(Industrial application fields)

The present invention concerns a non-aqueous electrolyte secondary battery, especially the improvement of its cathode.

[0002]

(Prior art)

A non-aqueous electrolyte secondary battery which possesses a cathode made of lithium or a lithium compound is expected to yield a high voltage and a high energy density, and accordingly, vigorous studies are being conducted on it. Oxides of transition metals such as LiCoO_2 , V_2O_3 , Cr_2O_3 , MnO_2 , TiS_2 , MoS_2 , etc. and chalcogen compounds have heretofore been known as anodic active materials. They are characterized by laminar or tunneled structure in possession of a crystalline structure which permits the entry and exit of lithium ions. Metallic lithium, on the other hand, has been extensively investigated as cathodic active materials. During a recharge cycle, however, lithium becomes

deposited on the lithium surface in a branched fashion, which is problematic in that the recharge & discharge efficiency may deteriorate and/or that an internal short-circuit may be incurred as a result of contact with the anode.

[0003]

(Problems to be solved by the invention)

As a mechanism for solving these problems, the use of a lithium alloy sheet which is capable of inhibiting the branched growth of lithium and of storing and releasing lithium (e.g., separated-aluminum, etc.) as a cathode has been investigated. In a case where such a lithium alloy sheet is used and where advanced recharge & discharge cycles become repeated, however, the size reduction of the electrode occurs, which is problematic in terms of cycle performances. Measures for inhibiting the size reduction of the electrode by using an alloy obtained by adding other elements to aluminum as an electrode have therefore been proposed (e.g., respective Gazettes of Japanese Patent Application Publication Kokai Nos. Sho 62[1987]-119856 and Hei 4[1992]-109562, etc.). The performances have, however, yet to be sufficiently improved at present. The objective of the present invention is to provide, by solving these problems, a non-aqueous electrolyte secondary battery which exhibits excellent recharge & discharge cycle performances.

[0004]

(Mechanism for solving the problems)

In the context of solving the aforementioned problems, the present invention is characterized by the fact that, in a non-aqueous electrolyte secondary battery in possession of a rechargeable and/or dischargeable anode, a non-aqueous electrolyte, and a rechargeable and/or dischargeable cathode, an Al-Si-Fe alloy which is capable of storing and releasing lithium in a reversible fashion is used as said cathode.

[0005]

(Functions)

To begin with, the hardness of the Al becomes fortified by the use of an alloy obtained by adding Si and Fe to Al, based on which the mechanical strengths become improved. An effect of inhibiting the size reduction in response to repeated recharge & discharge cycles can accordingly be achieved. In a case where an Al-Si or Al-Fe alloy is used, however, it is impossible to achieve a sufficient effect, and therefore, it is necessary to add both elements simultaneously. Si is, unlike Fe, endowed with a function of storing lithium similar to that ascribed to Al, based on which effects not only of upgrading the hardness but also of inhibiting the lithium storage capacity loss per unit alloy weight which would otherwise accompany the addition thereof can be achieved. As far as the addition ratios are concerned, it is desirable that the respective ratios of Si and Fe with respect to

the total weight of the Al-Si-Fe alloy to be designated within ranges of 1 ~ 50% and 0.1 ~ 8%. In a case where the respective quantitative ratios of Si and Fe are lower than 1% and 0.1%, the mechanical properties become insufficient, due to which it becomes impossible to obtain a sufficient cycle life. Conversely, as far as excessively high addition ratios are concerned, even in a case where the ratio of Si exceeds 50%, no further improvement of the cycle performance becomes acknowledged. In a case where the ratio of Fe exceeds 8%, furthermore, the cycle life becomes shortened due presumably to a diminished lithium storage capacity per unit alloy weight.

[0006]

This Al-Si-Fe alloy, on the other hand, is hard, and therefore, it may be difficult to process it into a sheet with a thickness of several hundred μm by means of a rolling mechanism of the prior art in some cases. In a case where the aforementioned alloy is processed into a powder and where an electrode is constituted by mixing it with a carbonaceous material and a binder, however, an electrode with a thickness of up to several hundred μm or so can be prepared, based on process-related problems can be solved.

[0007]

(Application examples)

In the following, an application example of the present invention will be explained in detail. Attempts were made, in the

context of evaluating the performances of an Al-Si-Fe alloy, to prepare the coin-shaped battery shown in Figure 1 and to investigate its performances. LiMn_2O_4 was used as an anodic active material endowed with reversible recharge & discharge attributes. 7 g of acetylene black, which served as an electroconductivizing agent, and 7 g of polyethylene tetrafluoride, which served as a binder, were added to and mixed with 100 g of the anodic active material, as a result of which an anodic mixture was obtained. 1 g of said anodic mixture was compressively molded, as the anode (1), into a disc with a diameter of 17.5 mm and then configured at the center of the case (2). The separator (3) made of microporous polypropylene was placed above it, and a non-aqueous electrolyte was then dispensed as a liquid. Said non-aqueous electrolyte was obtained by solubilizing 1 mole/L of lithium perchlorate (LiClO_4) into a mixed solvent of ethylene carbonate and dimethoxyethane (volume ratio: 1 : 1).

[0008]

30 g of a graphite powder and 10 g of a styrene-butadiene rubber powder, which served as a binder, were mixed with an Al-Si-Fe alloy powder with an average particle size of 50 μm characterized by each of the compositions shown in Table I, as a result of which a cathodic mixture was obtained. 0.1 g of this mixture was compressively molded, as the cathode (4), into a disc with a diameter of 17.5 mm. This cathode was placed above the separator, and after the area above it had been sealed with the sealing sheet (6), wherein the gasket (5) made of polypropylene

was attached to the outer circumference thereof, a battery was obtained. As a comparative example, a battery equipped with a cathode constituted by using an Al powder, Al-Fe alloy powder, or Al-Si alloy powder was also prepared.

[0009]

These batteries were subjected to recharge & discharge cycles at a current of 2 mA within a voltage range of 4.2 ~ 3 V. The cycle No. at which the discharge capacity dropped to 50% of the initial discharge capacity is shown in Table I as well as Figures 2 and 3.

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Table I: Recharge & discharge cycle Nos.

Fe ratio (wt%)	Si ratio (wt%)					
	0	1.0	10	30	50	60
0	56	68	75	85	91	92
0.1	60	140	163	191	209	210
1.0	65	153	173	209	216	210
5.0	70	165	180	232	242	240
8.0	79	164	182	235	245	244
15	72	120	125	130	135	136

[0011]

As Table I and Figures 2 & 3 indicate, the cycle performances become improved as the Si internalization ratio within the cathodic alloy increases, and the cycle performances become upgraded up to a ratio of 50 wt% or so. Virtually no improvements of the cycle performances are observed past 50 wt%. With regard to Fe, too, the cycle performances become improved as its internalization ratio increases up to 8 wt% or so. Conversely, the capacity begins to diminish past 15 wt%. The cycle performances, furthermore, become greatly improved by adding Si and Fe simultaneously.

[0012]

It can be inferred from the foregoing results that the cycle performances can be significantly improved by using an Al-Si-Fe alloy which includes both Si and Fe at appropriate ratios. Since the respective melting points of Si and Fe are higher than that of Al, the melting temperature during an alloy preparation operation can be lowered by minimizing the addition ratios of both, which is advantageous in terms of cost. For these reason, it is desirable for the respective addition ratios of Si and Fe with respect to the total weight of the Al-Si-Fe alloy to be designated within ranges of 1 ~ 50% and 0.1 ~ 8%. Incidentally, an application embodiment of a coin-shaped battery has been explained in the aforementioned application example, but it goes without saying that the present invention is not limited to this structure and

that similar effects can be achieved by designing secondary batteries of other shapes (e.g., cylindrical, angular, flat, etc.).

[0013]

(Effects of the invention)

As has been shown above, as far as the present invention is concerned, a secondary battery endowed with excellent recharge & discharge cycle performances can be obtained by using, as a cathode, an Al-Si-Fe alloy which is capable of storing and releasing lithium in a reversible fashion.

Brief explanation of the figures

Figure 1: A diagram which shows a lengthwise cross-sectional view of the non-aqueous electrolyte secondary battery of an application example of the present invention.

Figure 2: A diagram which shows the relationship between the Si internalization ratios of cathodic alloys and cycle performances of secondary batteries.

Figure 3: A diagram which shows the relationship between the Fe internalization ratios of cathodic alloys and cycle performances of secondary batteries.

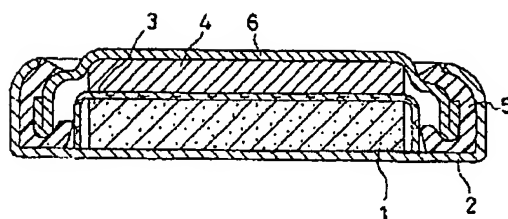
(Explanation of notations)

(1): Anode; (2): Case; (3): Separator; (4): Cathode; (5): Gasket; (6): Sealing sheet.

Figure 1

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【図1】

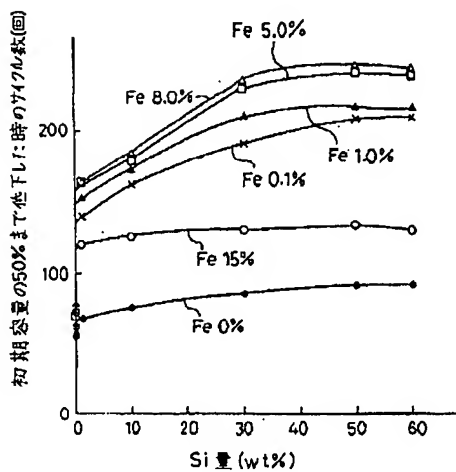


1: 正極
3: セパレーター
4: 負極

[(1): Anode; (3): Separator; (4): Cathode]

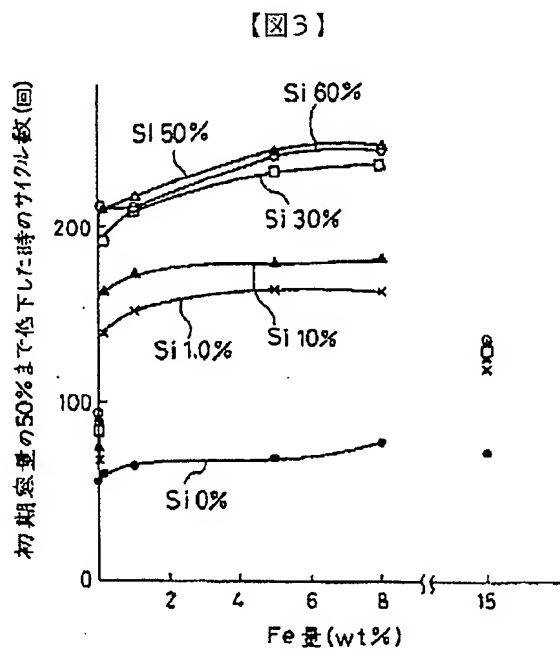
Figure 2

【図2】



[(1): Cycle No. at which the discharge capacity dropped to 50% of the initial discharge capacity (N); (2): Si ratio (wt%)]

Figure 3



[(1): Cycle No. at which the discharge capacity dropped to 50% of the initial discharge capacity (N); (2): Fe ratio (wt%)]